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(54) **Polyethylene compositions for rotomolding**

(57) A polymer composition suitable for rotomoulding comprising

I) an ethylene homopolymer or copolymer with at least one other C₃₋₁₀ α -olefin, having a melt flow rate of 0.5 to 30, a molecular weight distribution (Mw/Mn) of less than 4, an Mw of 50,000 to 110,000, a density of 0.940 g/cm³ to 0.970 g/cm³ and a melting point of 100 to 145°C;

OR

I) a propylene homopolymer or copolymer with at least one other C₂₋₁₀ α -olefin, having a melt flow rate of 0.5 to 30, a molecular weight distribution (Mw/Mn) of less than 4, an Mw of 150,000 to 300,000, and a melting point of 100 to 170°C;

and

II) an ethylene homo or copolymer with at least one other C₃₋₁₀ α -olefin, having a melt flow rate of within 40% of the melt flow rate of component (I), a molecular weight distribution of (Mw/Mn) of less than

4, an Mw of within 30% of the Mw of component (I), a density of 0.880 g/cm³ to 0.940 g/cm³ said density being at least 0.010 g/cm³ less than the density of component (I) and a melting point of at least 5°C less than that of component (I);

OR

II) a propylene homo or copolymer with at least one other C₂₋₁₀ α -olefin having a melt flow rate of within 40% of the melt flow rate of component (I), a molecular weight distribution of (Mw/Mn) of less than 4, an Mw of within 30% of the Mw of component (I), and a melting point of at least 10°C less than that of component (I).

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Description

[0001] This invention relates to the use of a particular polymer composition in for example, rotational moulding as well as to the polymer composition itself, to rotomoulding processes using the same and to rotomoulded articles made from the polymer composition. More specifically, the invention concerns the use of a polymer composition which comprises at least two components formed by single site catalysis having particular molecular weight distributions, comonomer compositions and densities.

[0002] Rotational moulding is a moulding process in which a particulate polymer, the moulding powder, is filled into a mould which is placed into an oven and rotated so that the polymer melts and coats the inside surface of the mould. In order to ensure that the moulded product is defect free, the moulding powder must have a relatively small particle size and should preferably be uniform in particle size and composition. Where, as is normal, the moulding powder has to contain colouring agents or other additives, e.g. stabilisers, the moulding powder is conventionally produced by grinding polymer pellets extruded from stabilised reactor grain powder to the correct particle size for rotation of moulding, usually this the colours or other additives being added in with the polymer pellets are mixed into the ground and moulding powder.

[0003] A wide variety of articles may be prepared by rotational moulding. In particular rotational moulding is used in the manufacture of large objects such as liquid containers, e.g. tanks, boats, as well as in a large number of household areas, e.g. in the manufacture of toys.

[0004] The nature of the polymer rotomoulded depends very much on the nature of the article to be made. For example, if a chemical tank is being made, then the polymer used should be one which is not degraded by the chemical and one which has particular mechanical properties so that the container does not break under stress. Polymers used for the manufacture of toys must be completely non-toxic and again must be strong to prevent breakage. Articles for outdoor use such as boats must also be resistant to degradation from by the elements, e.g. sunlight, rain, frost or seawater. The mechanical properties of the rotomoulding powders are therefore critical.

[0005] Another important property is rheology and it is also critical that this is favourable. Rheology is a measure of non-Newtonian solid flow and it is crucial that flow be within certain limits to ensure that product properties are ideal.

[0006] Moreover, when making objects where a well defined shape is required, it is also desired that the eventual rotomoulded product does not warp, i.e. that the sides of a product remain undistorted.

[0007] A variety of polymers may be successfully rotomoulded although homo and copolymers of ethylene and homo and copolymers of propylene may in particular be mentioned. However, the nature of the catalyst used to make the polymer has a significant bearing on the rotomouldability of the polymer.

[0008] In rotomoulding, polymers produced from single site catalysts give rise to products having excellent mechanical properties and enable rotomoulding to be carried out over a much shorter period of time. Polymers produced from single site catalysts tend to have a narrow molecular weight distribution and copolymers produced from single site catalysts tend to have narrow comonomer distribution. These properties gives rise to increased environmental stress cracking resistance and improvements in other mechanical properties.

[0009] However, the narrow distribution of comonomers as compared to a Ziegler-Natta produced polymer, results in a much narrower melting and crystallisation behaviour. The sharp melting behaviour makes the polymer very sensitive to processing temperature and, without wishing to be limited by theory, it is believed that this causes severe warpage in rotomoulding products. Hence, the mechanical property benefits of using a polymer made by single site catalysis are offset by increased warpage.

[0010] Polymers produced using Ziegler-Natta catalysts have much broader melting/crystallisation windows than polymers made by single site catalysis and hence tend to produce rotomoulding products with much less warpage. However, due to the broad comonomer distribution and broad molecular weight distribution mechanical properties, especially ESCR and rheology are not so favourable.

[0011] There still remains therefore, the need to find a polymer suitable for rotational moulding that can give rise to products having both low warpage and excellent rheological and mechanical properties.

[0012] It has now been surprisingly found that by forming, e.g. blending, a particular mix of polymers, preferably made by single site catalysis a polymer composition may be produced which not only has excellent mechanical and rheological properties but also does not warp after rotomoulding since its processing window is broadened. A blend of polymers having, depending on the monomers involved, similar molecular weights and similar melt flow rates but different densities, melting points or comonomer distributions has surprisingly been found to give rise to a composition which shows an overall narrow molecular weight distribution and hence excellent mechanical and rheological properties and has a broadened processing window which eliminates warpage normally associated with single site materials.

[0013] Hence, viewed from one aspect the invention provides a polymer composition suitable for rotomoulding comprising

l) a first ethylene homo or copolymer with at least one other C₃₋₁₀ α -olefin, having a melt flow rate (MFR) of 0.5 to

30, preferably 3 to 15, especially 6 to 8, a molecular weight distribution (Mw/Mn) of less than 4, preferably less than 3.5, especially less than 3, an Mw of 50,000 to 110,000, a density of 0.940 g/cm³ to 0.970 g/cm³ and a melting point of 100 to 145°C;

OR

I) a propylene homo or copolymer with at least one other C₂₋₁₀ α-olefin, having a melt flow rate of 0.5 to 30, preferably 3 to 15, especially 6 to 8, a molecular weight distribution (Mw/Mn) of less than 4, preferably less than 3.5, especially less than 3, an Mw of 150,000 to 300,000, and a melting point of 100 to 170°C;

and

II) a second ethylene homo or copolymer with at least one other C₃₋₁₀ α-olefin, having a melt flow rate of within 40%, preferably 20% of the melt flow rate of component (I), a molecular weight distribution of (Mw/Mn) of less than 4, an Mw of within 30%, preferably 20% of the Mw of component (I), a density of 0.880 g/cm³ to 0.940 g/cm³ said density being at least 0.010 g/cm³ less than the density of component (I) and a melting point of at least 5°C, preferably at least 10°C less than that of component (I);

OR

II) a propylene homo or copolymer with at least one other C₂₋₁₀ α-olefin having a melt flow rate of within 40%, preferably 20% of the melt flow rate of component (I), a molecular weight distribution of (Mw/Mn) of less than 4, an Mw of within 30%, preferably 20% of the Mw of component (I), and a melting point of at least 10°C less than that of component (I).

[0014] Viewed from another aspect the invention provides a polymer composition suitable for rotomoulding comprising as hereinbefore described wherein said composition has a molecular weight distribution (Mw/Mn) of less than 4, an Mw of within 30%, preferably 20% of the Mw of component (I), and an Mn within 30%, preferably 20% of the Mw of component (I).

[0015] In an especially preferred embodiment, the invention provides a polymer composition suitable for rotomoulding comprising

I) an ethylene homopolymer having a melt flow rate of 0.5 to 30, preferably 3 to 15, especially 6 to 8, a molecular weight distribution (Mw/Mn) of less than 4, preferably less than 3.5, especially less than 3, an Mw of 50,000 to 110,000, a density of 0.940 g/cm³ to 0.970 g/cm³ and a melting point of 100 to 145°C;

and

II) an ethylene copolymer with at least one C₃₋₁₀ α-olefin having a melt flow rate of within 40%, preferably 20% of the melt flow rate of component (I), a molecular weight distribution of (Mw/Mn) of less than 4, an Mw of within 30%, preferably 20% of the Mw of component (I), a density of 0.880 g/cm³ to 0.940 g/cm³, preferably 0.910 g/cm³ to 0.930 g/cm³ said density being at least 0.010 g/cm³ less than the density of component (I) and a melting point of at least 10°C less than that of component (I).

[0016] Viewed from another aspect the invention provides the use of a polymer composition as hereinbefore described in rotomoulding.

[0017] Viewed from yet another aspect the invention provides a process for the preparation of an article comprising rotomoulding a composition as herein before defined.

[0018] Viewed from yet another aspect the invention provides an article comprising a polymer composition as hereinbefore described, especially a rotomoulded article.

[0019] Viewed from yet another aspect the invention provides a process for the preparation of a polymer composition as hereinbefore described wherein said composition is produced in at least two reactors in cascade or parallel, e.g. two slurry phase reactors or two gas phase reactors, especially a slurry phase followed by gas phase reactor.

[0020] Viewed from another aspect the invention provides a process for the preparation of a polymer composition as hereinbefore described comprising blending components (I) and (II) in conventional blending apparatus, preferably a micropellet extruder.

[0021] Viewed from another aspect the invention provides a process for the preparation of a polymer composition as hereinbefore described said process comprising the use of at least two catalysts, preferably metallocene catalysts, e.g. a dualsite catalyst preferably a dualsite metallocene catalyst.

[0022] Unless otherwise stated densities are measured according to ISO 1183-1987(E). MFR is measured according to ISO 1133-1997 (D -for PE/M for PP). The melting point of polyethylene is measured by heating the polymer from room temperature to 200°C at a heat rate of 10°C/min. The polymer is maintained at 200°C for 5 mins and then cooled to -10°C at a cool rate of 10°C/min and maintained at -10°C for 1 minute. The polymer is then heated to 200°C at a heat rate of 10°C/min and the melting point is taken on this second heat run. For polypropylene the procedure is identical except that heating takes place to 225°C and cooling is effected to 20°C. GPC analyses were carried out

under the following conditions:

Equipment: Waters 150 CV plus no. 1115

Detector: Refractive Index (RI) and Viscosity detector Calibration: Narrow molecular weight distribution PS 1. Columns: 3 x HT6E styragel from Waters (140°C).

[0023] Components (I) and (II) may be copolymers of ethylene or propylene with at least one other C₂₋₁₀ α -olefin. Suitable comonomers include ethylene, propylene, 1-butene, 1-hexene, 1-octene etc. Clearly, ethylene is only a suitable comonomer when the major monomer is propylene and propylene is only a suitable comonomer where the major monomer is ethylene. Diolefins may also be employed as comonomers especially those having two terminal double bonds, e.g. butadiene. In a preferred embodiment, where component (I) or (II) is a copolymer, it is a copolymer of ethylene with octene, butene or hexene, especially butene or hexene.

[0024] Component (I) or (II) may also be a homopolymer of propylene having no or only a few crystallinity disrupting units, e.g. less than 5 units per 100 propylene linkages. By crystallinity disrupting units it is meant a unit that disrupts the regular structure of the polymer, i.e. an atactic unit in syndiotactic or isotactic propylene polymers. In one embodiment, both components (I) and (II) should be propylene homopolymers in which component (I) is preferably a syndiotactic or isotactic propylene component and component (II) is preferably an amorphous propylene homopolymer. In a less preferred embodiment component (I) may be a polypropylene homopolymer and component (II) may be a propylene copolymer.

[0025] In another less preferred embodiment both components may be ethylene homopolymers in which component (II) comprises a high degree of short chain branching.

[0026] In a final and most preferred embodiment, component (I) may be an ethylene homopolymer and component (II) may be an ethylene copolymer.

[0027] The polymer components (I) and (II) should preferably have similar melt flow rates, i.e. the melt flow rate of component (II) should not differ from the melt flow rate of component (I) by greater than 40%, e.g. 20%, preferably no more than 10%, especially no more than 5%. The melt flow rate of the components should be in the range 0.5 to 30, preferably 1 to 20, more preferably 3 to 15, e.g. 4 to 10, especially 6 to 8, most especially about 6. In a highly preferred embodiment both components (I) and (II) have a MFR of about 6.

[0028] The melt flow rate of the entire composition should also be in the range 0.5 to 30, preferably 1 to 20, more preferably 2 to 15, e.g. 4 to 10, especially 6 to 8, most especially about 6.

[0029] The molecular weight distribution (MWD) of both components should be approximately the same, e.g. within 10%, and the MWD must be narrow, e.g. an (Mw/Mn) of less than 4, preferably less than 3.5, especially less than 3. The MWD of the entire composition should also preferably be less than 4, especially less than 3.5.

[0030] Whilst the Mw and Mn ranges may vary within wide limits the Mw/Mn ratio remains low, i.e. less than 4. In a preferred embodiment the Mw and Mn of both components are also similar. For a polyethylene homopolymer or copolymer suitable Mw values are in the range 50000 to 110000, especially 65000 to 85000. For a propylene homopolymer or copolymer suitable Mw values are Mw of 150,000 to 300,000. The Mw of component (II) should be within 30%, preferably 20% of the Mw of component (I).

[0031] For compositions based on ethylene, the densities of the two components should be different, i.e. component (II) should have a density at least 0.010 g/cm³, especially 0.020 g/cm³ different from component (I). For ethylene homo and copolymers, preferably component (I) should have a density in the range 0.940 to 0.970 g/cm³ and component (II) should have a density in the range of 0.880 to 0.940 g/cm³, preferably in the range 0.910 g/cm³ to 0.930 g/cm³, said density preferably being at least 0.010 g/cm³ less than the density of component (I).

[0032] For compositions based on ethylene, the density of the entire composition is preferably in the range 0.925 to 0.950 g/cm³, preferably 0.930 to 0.940 g/cm³.

[0033] The two components must also have different crystallinity properties, i.e. components (I) and (II) should have different melting points. This may be achieved by providing copolymers with differing comonomer contents or for a composition containing only homopolymers by providing a polymer having differing numbers of crystallinity disrupting units (e.g. short chain branches).

[0034] Where component (I) is an ethylene homo or copolymer it may have a melting point of 100 to 145°C. Where component (I) is a propylene copolymer or propylene homopolymer it should have a melting point of 100 to 170°C.

[0035] Component (II) should have a melting point which differs from that of component (I) by at least 5°C, preferably at least 10°C, especially at least 20°C. In the case of a propylene homopolymer, component (II) may also be amorphous and may therefore have no defined melting point.

[0036] Thus an especially preferred composition according to the invention is a composition in which component (I) is an ethylene homopolymer having an MFR of 6 to 8, a molecular weight distribution of less than 3, an Mw of 65,000 to 100,000, an Mn of 20,000 to 60,000, a density of 0.945 to 0.970 g/cm³ and a melting point of 125 to 135°C; and component (II) is an ethylene copolymer with hexene having an MFR of 6 to 8, a molecular weight distribution of less

than 3, an Mw of 65,000 to 100,000, an Mn of 20,000 to 60,000, a density of 0.910 to 0.940 g/cm³ and a melting point of 100 to 125°C.

[0037] In order to prepare the required polymer for rotomoulding, components (I) and (II) may be blended using conventional blending or compounding technology. The components (I) and (II) may be mixed in any convenient ratio to ensure that the desired properties are obtained. Preferably however, the ratio of component (I) to (II) is from 95:5 to 5:95, preferably 9:1 to 1:9, especially 4:1 to 1:4, more especially 1:2 to 2:1.

[0038] Components (I) and (II) may also be used in conjunction with other polymers in the blend such as rotomoulding polymer grades and some Ziegler-Natta polymers. Moreover, it is within the scope of the invention to use a further polymer component (III) which also has a MWD and MFR similar to components (I) and (II) but has a still different comonomer distribution hence producing a multimodal comonomer distribution.

[0039] The polymer composition described above gives rise to rotomoulded articles with excellent mechanical and rheological properties and low warpage.

[0040] The components are preferably produced using a single site catalyst, e.g. metallocene catalyst or potentially a dualsite catalyst. However, where component (I) or (II) is a homopolymer Ziegler-Natta catalysis may be employed. This is not however, preferred. Suitable metallocene catalysts for use in the invention may be any conventional metallocene catalyst. As used herein, the term metallocene is used to refer to all catalytically active metal: η -ligand complexes in which a metal is complexed by one, two or more open chain or closed ring η -ligands. The use of bridged bis- η -ligand metallocenes, single η -ligand "half metallocenes", and bridged η - σ ligand "scorpionate" metallocenes is particularly preferred. The metal in such complexes is preferably a group 4A, 5A, 6A, 7A or 8A metal or a lanthanide or actinide, especially a group 4A, 5A or 6A metal, particularly Zr, Hf or Ti. The η -ligand preferably comprises an η^4 or η^5 open chain or an η^5 -cyclopentadienyl ring, optionally with a ring or chain carbon replaced by a heteroatom (e.g. N, B, S or P), optionally substituted by pendant or fused ring substituents and optionally linked by bridge (e.g. a 1 to 4 atom bridge such as (CH₂)₂, C(CH₃)₂ or Si(CH₃)₂) to a further optionally substituted homo or heterocyclic cyclopentadienyl ring. The ring substituents may for example be halo atoms or alkyl groups optionally with carbons replaced by heteroatoms such as O, N and Si, especially Si and O and optionally substituted by mono or polycyclic groups such as phenyl or naphthyl groups. Suitable η -ligands, include those of formula II discussed above. Examples of such homo or heterocyclic cyclopentadienyl ligands are well known in the art (see e.g. EP-A-416815, WO96/04290, EP-A-485821, EP-A-485823, US-A-5276208 and US-A-5145819).

[0041] Besides the η -ligand, the metallocene complex used according to the invention may include other ligands; typically these may be halide, hydride, alkyl, aryl, alkoxy, aryloxy, amide, carbamide or other two electron donor groups. Any hydrocarbyl ligand here will generally contain up to 20 carbons, preferably up to 10 carbons, e.g. up to 6 carbons.

[0042] Metallocene catalysts are conventionally employed in the presence of a cocatalyst. Suitable cocatalysts are well known and include alkyl metal compounds, in particular alumoxanes. Suitable alumoxanes include C₁₋₁₀ alkyl alumoxanes, e.g. methyl alumoxane (MAO) and isobutyl alumoxanes (e.g. tetra and hexaisobutyl alumoxane, TIBAO and HIBAO), especially MAO. Alumoxane co-catalysts are described by Hoechst in WO-A-94/28034. These are considered cyclic or cage like oligomers having up to 40, preferably 3 to 20, -[Al(R')O]- repeat units (where R' is hydrogen, C₁₋₁₀ alkyl, preferably methyl, or C₆₋₁₈ aryl or mixtures thereof).

[0043] If desired the metallocene or metallocene/cocatalyst mixture may be used in unsupported form or it may be precipitated and used as such. However the metallocene or its reaction product with the cocatalyst is preferably introduced into the polymerization reactor in supported form, e.g. impregnated into a porous particulate support, as is well known in the art.

[0044] The particulate support material used is preferably an organic or inorganic material, e.g. a polymer (such as for example polyethylene, polypropylene, an ethylene-propylene copolymer, another polyolefin or polystyrene or a combination thereof). Such polymeric supports may be formed by precipitating a polymer or by a prepolymerization, eg of monomers used in the polymerization for which the catalyst is intended. However, the support is especially preferably a metal or pseudo metal oxide such as silica, alumina or zirconia or a mixed oxide such as silica-alumina, in particular silica, alumina or silica-alumina.

[0045] Especially preferably the support is a porous material so that the metallocene may be loaded into the pores of the support, e.g. using a process analogous to those described in WO94/14856 (Mobil), WO95/12622 (Borealis) and WO96/00243 (Exxon). The particle size is not critical but is preferably in the range 5 to 200 μ m, more preferably 10 to 80 μ m.

[0046] Before loading, the particulate support material is preferably calcined, i.e. heat treated, preferably under a non-reactive gas such as nitrogen. This treatment is preferably at a temperature in excess of 100°C, more preferably 200°C or higher, e.g. 200-800°C, particularly about 300°C. The calcination treatment is preferably effected for several hours, e.g. 2 to 30 hours, more preferably about 10 hours.

[0047] A cocatalyst, e.g. an alumoxane or an ionic catalyst activator (such as a boron or aluminium compound, especially a fluoroborate) may also be mixed with or loaded onto the catalyst support material. This may be done subsequently or more preferably simultaneously to loading of the metallocene, for example by including the cocatalyst

in the solution of the metallocene or, by contacting the metallocene loaded support material with a solution of the cocatalyst or catalyst activator, e.g. a solution in an organic solvent. Alternatively however, any such further material may be added to the metallocene loaded support material in the polymerization reactor or shortly before dosing of the catalyst material into the reactor.

[0048] In this regard, as an alternative to an alumoxane it may be preferred to use a fluoroborate catalyst activator, especially a $B(C_6F_5)_3$ or more especially a $\ominus B(C_6F_5)_4$ compound, such as $C_6H_5N(CH_3)_2H:B(C_6F_5)_4$ or $(C_6H_5)_3C:B(C_6F_5)_4$. Other borates of general formula $(cation^+)_a(borate^-)_b$ where a and b are positive numbers, may also be used.

[0049] Both components (I) and (II) may be prepared simultaneously using a dualsite catalyst, i.e. a catalyst carrying two active metallocene sites on a single support, one site designed to give a component (I) and the other designed to give component (II).

[0050] The polymerisation is typically conducted in the presence of a diluent. As a diluent, a linear, branched or cyclic saturated hydrocarbon such as butane, propane, pentane, hexane, heptane, octane, cyclohexane or methylcyclohexane may be used.

[0051] Polymerisation to produce the polymer for use in the invention may take place in the slurry, solution or gas phase. Slurry phase polymerisation can be conducted under standard slurry conditions.

[0052] For slurry reactors, the reaction temperature will generally be in the range 60 to 110°C (e.g. 80-110°C), the reactor pressure will generally be in the range 5 to 80 bar (e.g. 25-65 bar), and the residence time will generally be in the range 0.3 to 5 hours (e.g. 0.5 to 2 hours). The diluent used will generally be an aliphatic hydrocarbon having a boiling point in the range -70 to +100°C, especially isobutane or propane.

[0053] For solution phase reactors, the reaction temperature used will generally be in the range 130 to 270°C, the reactor pressure will generally be in the range 20 to 400 bar and the residence time will generally be in the range 0.1 to 1 hour. The solvent used will commonly be a hydrocarbon with a boiling point in the range 80-200°C.

[0054] For gas phase reactors, the reaction temperature used will generally be in the range 60 to 115°C (e.g. 70 to 110°C), the reactor pressure will generally be in the range 10 to 25 bar, and the residence time will generally be 1 to 8 hours. The gas used will commonly be a non-reactive gas such as nitrogen together with monomer (e.g. ethylene).

[0055] In order to ensure that copolymer particles are in the correct size for rotational moulding the products of any polymerisation reaction may be converted to powder form or pelletized to a particle size of approximately 0.1 to 0.5 mm, preferably 0.3 mm using standard technology. Hence, suitably sized pellets may be prepared by grinding.

[0056] Alternatively micropellets may be produced using the technique described in WO 00/35646 which is hereby incorporated by reference. By this method a mixture of polyolefin and optionally at least one additive is extruded in melt form through a die and pelletised to give particles having a particular size distribution. The particles are then dried to very low levels of moisture to improve rotomouldability.

[0057] Alternatively, the polymerisation, using a dualsite or multisite catalyst, can be set up such that the reactor powder is suitable for use without further manipulation. In one embodiment of the invention rotomoulding may be carried out by combining polymer powder with a masterbatch of UV-stabiliser-loaded polyolefin powder in line with the teaching of WO00/11065 which is hereby incorporated by reference.

[0058] The polymer powder or pellets can comprise any standard additives e.g. one or more selected from colouring agents, stabilisers, antioxidants, UV-absorbers, anti-static agents, lubricants and fillers.

[0059] Rotational moulding may take place under standard conditions. The polymer powder is placed in the mould which is then transferred to an oven and rotated, preferably about two axes to distribute the polymer powder over the hot surfaces of the mould. The heating cycle is continued until all of the powder has melted and formed a thick, continuous layer within the mould. The mould is then removed from the oven and cooled until the resin has solidified. The moulded part is then removed.

[0060] The length of time which the mould must be heated depends on the nature of the article being moulded, the amount of resin present and the temperature of the oven. Typical rotomoulding temperatures are 230°C to 350°C, more particularly 260°C to 320°C. Heating time is chosen such that the inner air temperature in the mould is 160°C to 300°C, more preferably 170°C to 250°C. This temperature can be measured using a Rotolog® or similar equipment to monitor the temperature or it may be chosen based on previous experience. Cooling may be carried out under a stream of air, water spray or mist or simply in ambient air at room temperature. A combination of these methods may also be employed. Preferably cooling is achieved using a combination of blown air followed by ambient air or just blown air. Cooling times are normally of similar magnitude to heating times or slightly longer. Slow cooling reduces the amount of warpage present in a rotomoulded article however, it is a purpose of the invention to provide polymer compositions which can be cooled more rapidly without increases in warpage compared to conventional single site polymers. The moulded tank may be removed from its mould at any convenient time although it is preferred if it is removed when it has cooled to a temperature of 60°C to 100°C.

[0061] The skilled artisan is able to manipulate the temperature, time and rotation speed/ratio within a rotomoulding apparatus to ensure that well-formed moulded articles are produced.

[0062] Particularly preferred rotomoulding conditions are Rotation Speed 9/1.4 RPM; heating for 13 minutes in oven

at 270°C; fan assisted cooling for 10 minutes followed by ambient air cooling for 6 minutes.

[0063] The polymer composition of the invention may also have utility outside the field of rotomoulding. It is envisaged that the composition may give benefits in thermoforming due to the broadened processing window which the polymers exhibit. In particular polymer compositions of this type may be useful in the replacement of PVC. The polymer compositions may also be useful in film and injection moulding applications and this forms a yet further aspect of the invention.

[0064] The invention will now be further illustrated with reference to the following non-limiting examples and figures.

Example 1

[0065] Two polymer components A and B were prepared as described in Annex 1 below. The catalyst used was made from (nBu-Cp)ZrCl₂ and MAO impregnated on a support of calcined silica. Polymerisations took place in a bench scale semibatch reactor with hydrogen premixed in Component A is an ethylene homopolymer made from a single site catalyst having a density of 0.957 g/cm³, an Mw of 77000, an Mn of 28000 giving a Mw/Mn of 2.7, a melting point of 132°C and a MFR of 6.

[0066] Component B is an ethylene/hexene copolymer having a density of 0.923 g/cm³, a Mw of 67000 and Mn of 31000 giving an Mw/Mn of 2.1, an MFR of 8 and a melting point of 120°C. These components were compounded together, optionally with further polyethylene reactor powders, RP1 and RP2 having a density of 0.934 g/cm³ and an MFR of 6 or a density of 0.939 g/cm³ and an MFR of 6 respectively. The polymer blend was completed by the addition of an antioxidant and a slip agent.

[0067] The polymer blends prepared are shown in Table 1 below:

Table 1

| Sample | Comp. A | RP1 | RP2 | Comp. B |
|--------|---------|-------|-----|---------|
| 934Y | 18% | 25% | 57% | - |
| 934A | 64% | - | - | 36% |
| 934B | 32% | 50% | - | 18% |
| 934C | 16% | 75% | - | 9% |
| 934D | 8% | 87.5% | - | 4.5% |
| 934Ref | - | 100% | - | - |

[0068] All blends were made to a total of 4 kg which resulted in approximately 3.8 kg of granules. These blends were then ground leaving at least 2.8 kg of powder. The overall density of each blend was 0.934 g/cm³, except 934Y which had a density of 0.940 g/cm³.

[0069] In addition, some commercially available polymer grades were readied for rotomoulding.

[0070] RM 8403, an ethylene/hexene copolymer available from Borealis A/S, is a polymer produced from a metallocene catalyst having the following properties: Mw=75000, Mn=34000, MWD=2.2, MFR 6, density 940 g/cm³, melting point 125°C, heat of fusion 194 J/g, cryst Temp 110°C, heat of cryst -158 J/g.

[0071] RM 8343, an ethylene/hexene copolymer available from Borealis A/S, is a polymer produced from a metallocene catalyst having the following properties: Mw 76000, Mn=34000, MWD=2.2 MFR 6, density 934 g/cm³, melting point 123°C, heat of fusion 176 J/g, cryst Temp 108°C, heat of cryst -156 J/g.

[0072] ME8152, an ethylene/butene copolymer available from Borealis A/S, is a polymer produced from a Ziegler-Natta catalyst having the following properties: Mw 101000, Mn 25000, MWD 4.1, MFR 3.5, density 934 g/cm³, melting point 125°C, heat of fusion 180 J/g, cryst Temp 110°C.

[0073] The properties of each blend are further explained in the table below

| | 934ref | 934A | 934B | 934C | 934D | 934Y |
|----------------|--------|-------|-------|-------|-------|-------|
| Density | 935.1 | 934.9 | 935.3 | 935.3 | 934.6 | 940.6 |
| Melt pt | 123.4 | 127 | 125 | 124.4 | 123.7 | 127 |
| heat of fusion | 163 | 163 | 164 | 164 | 160 | 182 |
| cryst T | 109 | 112.3 | 110.6 | 110 | 109.6 | 112.6 |
| heat of cryst | -155 | -151 | -153 | -154 | -148 | -173 |

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Example 2

[0074] Samples were rotomoulded under one or more of the following sets of conditions to form boxes.

Rotomoulding Serial 1

[0075] No preheating; Rotation Speed 9/1.4 RPM; heating for 13 minutes in oven at 270°C; fan assisted cooling for 10 minutes followed by 6 minutes ambient cooling in the absence of a fan. 700 g of polymer employed; Max mould temperature 227°C, mould temperature at start 35°C.

Rotomoulding Serial 3

[0076] Mould was preheated to 60°C; Rotation Speed 4/2; heating for 13 minutes in oven at 270°C; fan assisted cooling for 30 minutes. 700 g of polymer employed; Max mould temperature 227°C, mould temperature at start 60°C.

[0077] The boxes resulting from the rotomoulding were cubes having sides of approximately 20 cm. The edges of the boxes were trimmed.

Example 3

[0078] Warpage of the rotomoulded boxes was measured on five of the six cube walls (not the top wall). A ruler with a micrometer was used diagonally on each side of the box. Results are depicted in Table 2 relative to results achieved with ME8152.

Table 2

| Box | Average Warpage |
|------------------------|-----------------|
| ME8152 - Roto Serial 3 | 100% |
| ME8152 - Roto Serial 1 | 66% |
| RM8343 - Roto Serial 3 | 143% |
| RM8343 - Roto Serial 1 | 92% |
| 934A - Roto Serial 3 | 72% |
| 934A - Roto Serial 1 | 38% |

[0079] These results are graphically depicted in Figure 1.

Example 4

[0080] Thickness variation in the walls of the boxes was measured by taking five wall thickness measurements from each side of the boxes. Average thickness variation is standard deviation for all points of each box relative to ME8152. The results are depicted in Table 3 below.

Table 3

| Box | Thickness variation |
|------------------------|---------------------|
| ME8152 - Roto Serial 3 | 100% |
| ME8152 - Roto Serial 1 | 38% |
| RM8343 - Roto Serial 3 | 115% |
| RM8343 - Roto Serial 1 | 33% |
| 934A - Roto Serial 3 | 53% |
| 934A - Roto Serial 1 | 59% |

[0081] The data collected to obtain these results is shown in the attached Annex 2 in which 9_1.4 std represents rotomoulding Serial 1 and 4_2 full cool represents rotomoulding serial 3.

Discussion

[0082] Blends with the broadest comonomer distribution have significantly less warpage and thickness variation than the reference materials. Moreover, an analysis of the crystal lattice structure of 934A reveals a much finer crystal structure which should make the material more robust to morphological changes. The appearance of the boxes made with 934A was also improved and fewer air bubbles are formed in the rotomoulded article.

Example 5

[0083] Mechanical Properties. The following tests were employed to test the mechanical properties of the boxes produced.

Tensile Modulus: ISO527-1 (1993)

Instrument Falling Weight (IFW) ISO 6603-2: 1989

[0084] Circular disks with diameter 60 mm are used with a hemispherical striker of mass 10 kg and 20 mm diameter. Falling height 1 m at a velocity of 4.4m/s at -20°C. Rupture was ductile.

ESCR - ASTM D1693-97/ISO 1872-2: 1997

[0085] Standardised specimens are notched and stressed before being lowered into a solution of detergent at 50°C. (Detergent 10% Antarox (Igepal) CO-630. Specimen thickness 2 mm. Examination every 4 hours and calculation is based on probability of 50% broken samples.

Density - ISO 1183: 1987

[0086]

| | | | | | | | | | | | |
|---------------------------|-----------------------|------|----------|--------|--------|--------|--------|--------|--------|--------|--------|
| Mechanical data: | | | 934- Ref | 934- A | 934- B | 934- C | 934- D | 934- Y | RM8343 | RM8403 | ME8152 |
| ESCR | 10% F50 | | 33 | 24 | 21 | 25 | 36 | 10 | | | |
| Series 1 | | | | | | | | | | | |
| 9/1,4 13-10-6 | | | | | | | | | | | |
| Tensile properties | Tensile modulus | Mpa | 620 | 680 | 660 | 650 | 620 | 800 | 585 | 710 | 600 |
| | Stress at yield | Mpa | 18 | 18 | 18 | 18 | 18 | 21,5 | 17,5 | 20 | 17 |
| | Strain at yield | % | 13 | 11 | 12 | 12 | 12 | 11 | 13 | 12 | 13 |
| FWI at-20°C | Max force | N/mm | 1430 | 1390 | 1400 | 1410 | 1410 | 1470 | 1425 | 1490 | 1310 |
| | Total energy at break | J | 19 | 19 | 19 | 19 | 19 | 19 | 19 | 20 | 15 |
| | Total deformation | mm | 24 | 24 | 24 | 25 | 24 | 23 | 24 | 23 | 22 |
| Density | | | 937,2 | 937,4 | | | | | 936 | | 933,4 |
| Series 2 | | | | | | | | | | | |
| 9/1,4 13-30 | | | | | | | | | | | |
| Tensile properties | Tensile modulus | Mpa | 630 | 670 | 630 | | | 755 | | 740 | 610 |
| | Stress at yield | Mpa | 18 | 18 | 18 | | | 21 | | 20,5 | 17 |
| | Strain at yield | % | 12 | 11 | 12 | | | 11 | | 13 | 13 |
| FWI at-20°C | Max force | N/mm | 1440 | 1420 | 1420 | | | 1470 | | 1480 | 1320 |
| | Total energy at break | J | 19 | 19 | 19 | | | 19 | | 18 | 16 |
| | Total deformation | mm | 24 | 24 | 24 | | | 23 | | 23 | 22 |
| Series 3 | | | | | | | | | | | |
| 4/2 13/30 | | | | | | | | | | | |
| Tensile properties | Tensile modulus | Mpa | 640 | 700 | 670 | 680 | 645 | 795 | 615 | 705 | 600 |
| | Stress at yield | Mpa | 18 | 18 | 18 | 18,5 | 18 | 22 | 17,5 | 20 | 16,5 |
| | Strain at yield | % | 11,5 | 11 | 12 | 12,5 | 12 | 11 | 12,5 | 12,5 | 11 |
| FWI at-20°C | Max force | N/mm | 1220 | 1190 | 1190 | 1210 | 1210 | 1270 | 1200 | 1260 | 1100 |
| | Total energy at break | J | 17 | 17 | 17 | 17 | 17 | 17 | 16 | 16 | 13 |

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(continued)

| | | | | | | | | | | |
|------------------|-------------------|----------|--------|--------|--------|--------|--------|--------|--------|--------|
| Mechanical data: | | 934- Ref | 934- A | 934- B | 934- C | 934- D | 934- Y | RM8343 | RM8403 | ME8152 |
| | Total deformation | 24 | 25 | 24 | 24 | 24 | 24 | 24 | 24 | 23 |
| | mm | | | | | | | | | |
| Density | | 936,8 | 937 | 9 | | | | 935,7 | | 927,5 |

[0087] 934Y has the most favourable tensile and impact properties but has lower ESCR. Overall, compositions of the invention show improved warpage, stiffness, morphology and comparable or improved ESCR. Grade 934A has also been found to have increased high temperature stiffness.

Example 6

[0088] The warpage and thickness data for rotomoulding serial 1 with all blends is displayed in Annex 3 directly and in comparison to RM8343. Data for serial 3 is displayed in Annex 4 directly and in comparison to RM8343. These results are graphically depicted in Figure 2.

[0089] As will be seen, the warpage results for the compositions 934Y, 934A, 934B, 934C and 934 D are better than the results obtained using the available commercial grades.

Example 7

[0090] The following metallocenes are used in this example. $\text{Me}_2\text{Si}(\text{9Flu})_2\text{ZrCl}_2$ (A-metallocene) which produces amorphous atactic polypropylene and $\text{rac Me}_2\text{Si}(\text{2MeIndenyl})_2\text{ZrCl}_2$ (B-metallocene) which produces isotactic polypropylene. These catalysts are available from Boulder.

Dualsite catalyst preparation

[0091] Preparation of catalyst "60/40" in the Table in Example 8 - A pretreated silica carrier, calcined at 600°C was transferred to a small bottle with stirrer bar. The carrier was wetted with toluene (5.5 ml per 2 g carrier). A solution of 2.5 ml of 30% MAO in toluene, 38.4 mg of A-metallocene and 33.4 mg of B-metallocene was prepared and stirred for 30 mins. This solution is added dropwise to 5.5 ml of toluene containing 2 g of silica carrier and stirred for 20 minutes and left overnight. The catalyst is then dried in nitrogen for 2 hours at 40°C.

[0092] The other catalysts in Example 8 were made analogously to "60/40" maintaining the total molar metallocene concentration constant.

Example 8

[0093] The dry catalyst is fed into a 2L reactor under nitrogen. 650 ml propylene is added to the reactor and pre-polymerisation is initiated for 8 minutes at 15°C. The temperature is rapidly raised to 70°C and polymerisation takes place in the absence of hydrogen.

[0094] The reactor conditions are described in the Table below.

| Run no | Temp. °C | Time | H ₂ | mg cat | weight polymer | Extra TEA, 1M (A54) | Dual site catalyst in mol% (B/A) |
|--------|----------|--------|----------------|--------|----------------|---------------------|----------------------------------|
| 6301 | 70 °C | 40 min | 0 | 220 | 200 g | 0,3ml | 100/0 |
| 6303 | 70°C | 60 min | 0 | 200 | 15 g | 0,1 ml | 0/100 |
| 6314 | 70°C | 30 min | 0 | 230 | 190 g | 0,25 ml | 90/10 |
| 6315 | 70°C | 30 min | 0 | 210 | 190 g | 0,25 ml | 60/40 |
| 6316 | 70°C | 60 min | 0 | 230 | 130 g | 0,25 ml | 20/80 |
| 6317* | 70-80 °C | 55 min | 0 | 210 | 175 g | 0,3 ml | 20/80 |

| | Mw | Mn | MWD |
|-------------------------|---------|--------|-----|
| 6301 whole polymer | 185 000 | 82 000 | 2,3 |
| 6301 crystalline phase. | 185 000 | 82 000 | 2,3 |
| 6303 whole polymer | 190 000 | 55 000 | 3,3 |
| 6303 XS phase | 185 000 | 55 000 | 3,3 |
| 6314 whole polymer | 190 000 | 80 000 | 2,4 |

(continued)

| | Mw | Mn | MWD |
|------------------------|---------|---------|-----|
| 6314 crystalline phase | 190 000 | 80 000 | 2,4 |
| 6315 whole polymer | 210 000 | 80 000 | 2,6 |
| 6315 crystalline phase | 210 000 | 100 000 | 2,1 |
| 6316 whole polymer | 240 000 | 105 000 | 2,2 |
| 6316 crystalline phase | 230 000 | 105 000 | 2,2 |

Results

[0095] The properties of the resulting polymers are described in the table below. The polymer components produced form a composition which is expected to be ideal for rotomoulding due to the almost identical Mw and Mn values but differing melting point properties of the isotactic and amorphous components.

[0096] Runs 6316 and 6317 give rise to a polymer composition having xylene soluble fractions of 16 and 19 wt% respectively. (The polymer is boiled in xylene at 137°C for 30 minutes, cooled filtered and the crystalline phase precipitated). The polymer compositions are surprisingly free-flowing powders and it is believed that never before have free flowing polypropylene polymer compositions been prepared having such high xylene soluble fractions. This forms a further aspect of the invention. The high xylene soluble fraction is believed to give rise to a softer polymer which may warp less on rotomoulding.

[0097] Thus viewed from a further aspect the invention provides a free-flowing polypropylene homopolymer powder having a xylene soluble fraction of at least 7 wt%, preferably at least 12 wt%.

[0098] Viewed from another aspect the invention provides a free flowing propylene homo or copolymer powder comprising components A and B wherein:

Component A has a crystalline melting point; and

Component B has a melting point at least 10°C lower than that of component A, preferably 30°C, especially component B is amorphous, has an Mn of at least 25000 g/mol, preferably at least 40000 g/mol and has a comonomer content of less than 20 wt%, preferably less than 5 wt%;

said powder having an Mw of at least 75000 g/mol, a xylene soluble fraction of at least 7 wt%, preferably at least 12 wt%.

[0099] The catalyst used to manufacture said free flowing powder is also new. Thus viewed from another aspect the invention provides a solid, preferably supported multisite catalyst comprising two metallocenes A' and B';

metallocene A' comprising two optionally substituted indenyl groups connection via the 1-position of the indenyl, said metallocene having C_s symmetry and preferably comprising a group 4A metal;

metallocene B' comprising two optionally substituted fluorenyl groups connection via the 1-position of the fluorenyl, said metallocene B' having C_s symmetry and preferably comprising a group 4A metal.

Annex IPREPARATION OF COMPONENTS A & B USING (nBu-Cp)₂ZrCl₂/MAO ON SILICA

| Cal temp (°C)/Loading (%) | 600/100 | 600/100 | 600/100 | 600/100 | 600/100 | 600/100 | 600/100 | 600/100 | 600/100 |
|--|-------------|---------|---------|---------|-------------|---------|---------|---------|---------|
| IMP | Dry-mix | Dry-mix | Dry-mix | Dry-mix | Dry-mix | Dry-mix | Dry-mix | Dry-mix | Dry-mix |
| Reac temp | 94 | 94 | 94 | 94 | 94 | 85 | 85 | 85 | 85 |
| Reac pres (bar) | 25,5 | 25,5 | 25,5 | 25,5 | 25,5 | 23,1 | 23,1 | 23,1 | 23,1 |
| Eten partial pressure (bar) | 7,5 | 7,5 | 7,5 | 7,5 | 7,5 | 7,5 | 7,5 | 7,5 | 7,5 |
| Eten H ₂ ratio (ppmH ₂) | 420 | 420 | 420 | 420 | 420 | 650 | 650 | 650 | 440 |
| C ₆ /Erene-Cascade (Wt%C ₈) | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 6,00 | 6,00 | 6,00 | 6,00 |
| TOTAL RUN TIME (min) | 60 | 60 | 60 | 60 | 60 | 60 | 60 | 60 | 60 |
| MFR2 (powder) | 6,1 | 6,4 | 6,8 | 6,2 | 6,2 | 8,1 | 8,5 | 8,3 | 6,5 |
| MFR21 (powder) | 95 | 105 | 121 | 103 | 103 | 123,0 | 122 | 120 | 110 |
| FFR (powder) | 15,6 | 16,4 | 17,8 | 16,6 | 16,6 | 15,2 | 14,4 | 14,5 | 16,9 |
| DENSITY (powder kg/dm ³) | 0,9573 | 0,9577 | 0,9563 | 0,9568 | 0,9568 | 0,9224 | 0,9214 | 0,9216 | 0,9245 |
| | COMPONENT A | | | | COMPONENT B | | | | |

ANNEX 2

9_1.4 std vs 4_2 full cool

Roto 1 vs Roto 3

| Material | 934_A1std | 934_A1c42 | RM8343std | RM8343c42 | ME8152std | ME8152c42 | Material | Box | 934_A1opt | 934_A1c4 | RM8343opt | RM8343c4 | ME8152opt | ME8152c4 |
|-------------|-----------|------------|------------|-------------|------------|-------------|-------------|-----------|-----------|----------|-----------|----------|-----------|----------|
| Warpage | | | | | | | Warpage | | | | | | | |
| Center | | | | | | | Center | | | | | | | |
| S2E | 0.45 | -0.5 | 0.34 | 0.48 | 1.04 | 1.82 | S2E | 0.234375 | -0.28042 | 0.177083 | 0.25 | 0.541657 | 1 | 1 |
| S3E | 1.61 | 1.5 | 2.16 | 4.71 | 1.9 | 1.9 | S3E | 0.644 | 0.8 | 0.88 | 1.884 | 0.76 | 1 | 1 |
| S4E | 0.67 | -1.1 | 1.5 | 1.28 | 1.68 | 1.34 | S4E | 0.5 | -0.82838 | 1.118403 | 0.955224 | 1.238808 | 1 | 1 |
| S5E | 1.4 | 1.6 | 2.75 | 4.88 | 1.71 | 2.66 | S5E | 0.528316 | 0.801504 | 1.038835 | 1.827088 | 0.842857 | 1 | 1 |
| S6E | 0.31 | 3.8 | 3.82 | 5.87 | 1.8 | 3.85 | S6E | 0.075948 | 0.862025 | 0.897089 | 1.488078 | 0.405083 | 1 | 1 |
| WAV(S1-S6)E | 0.886 | 1.058 | 2.112 | 3.44 | 1.682 | 2.474 | WAV(S1-S6)E | 0.388124 | 0.427648 | 0.863678 | 1.360481 | 0.63945 | 1 | 1 |
| S2max | 0.65 | 0.8 | 0.69 | 1.02 | 1.09 | 1.82 | S2max | 0.338542 | 0.418887 | 0.358373 | 0.53125 | 0.967708 | 1 | 1 |
| S3max | 1.61 | 1.5 | 2.15 | 4.71 | 1.9 | 2.3 | S3max | 0.644 | 0.8 | 0.88 | 1.884 | 0.76 | 1 | 1 |
| S4max | 0.69 | 1.2 | 1.72 | 1.28 | 1.78 | 1.34 | S4max | 0.514925 | 0.885522 | 1.283582 | 0.955224 | 1.335821 | 1 | 1 |
| S5max | 1.4 | 1.6 | 2.75 | 4.88 | 1.75 | 2.88 | S5max | 0.528316 | 0.801504 | 1.038835 | 1.827088 | 0.842857 | 1 | 1 |
| S6max | 0.34 | 3.8 | 4.01 | 5.87 | 1.8 | 3.95 | S6max | 0.088078 | 0.862025 | 0.91519 | 1.488078 | 0.405083 | 1 | 1 |
| WAV(S1-S6)M | 0.938 | 1.78 | 2.284 | 3.548 | 1.828 | 2.474 | WAV(S1-S6)M | 0.378143 | 0.719483 | 0.916117 | 1.434115 | 0.657235 | 1 | 1 |
| Thickness | | | | | | | Thickness | | | | | | | |
| 2.A | 3.55 | 3.55 | 3.64 | 3.62 | 3.43 | 3.69 | 2.A | 0.98208 | 0.86208 | 0.8645 | 0.88103 | 0.828338 | 1 | 1 |
| 2.B | 3.36 | 3.67 | 3.59 | 3.73 | 3.37 | 3.85 | 2.B | 0.872227 | 0.953247 | 0.932488 | 0.98831 | 0.875325 | 1 | 1 |
| 2.C | 3.48 | 3.78 | 3.89 | 3.89 | 3.77 | 4.01 | 2.C | 0.870324 | 0.937858 | 0.9202 | 0.870075 | 0.84015 | 1 | 1 |
| 2.D | 3.6 | 3.83 | 3.89 | 3.92 | 3.71 | 4.05 | 2.D | 0.888889 | 0.958025 | 0.911111 | 0.867901 | 0.816048 | 1 | 1 |
| 2.E | 3.37 | 3.48 | 3.58 | 3.66 | 3.56 | 4 | 2.E | 0.8425 | 0.885 | 0.885 | 0.865 | 0.885 | 1 | 1 |
| 3.A | 3.24 | 3.05 | 3.69 | 3.22 | 3.28 | 3.1 | 3.A | 1.045161 | 0.863871 | 1.030323 | 1.03871 | 1.058085 | 1 | 1 |
| 3.B | 3.24 | 3.34 | 3.47 | 3.17 | 3.18 | 3.16 | 3.B | 1.022152 | 1.058962 | 1.086101 | 1.003165 | 1.008328 | 1 | 1 |
| 3.C | 3.52 | 3.85 | 3.48 | 3.65 | 3.88 | 3.77 | 3.C | 0.933887 | 0.86817 | 0.823077 | 0.841845 | 0.878127 | 1 | 1 |
| 3.D | 3.55 | 3.74 | 3.43 | 3.54 | 3.51 | 3.87 | 3.D | 0.967302 | 1.018074 | 0.834605 | 0.864578 | 0.958403 | 1 | 1 |
| 3.E | 3.02 | 2.9 | 3.22 | 2.58 | 3.15 | 2.81 | 3.E | 1.037801 | 0.896584 | 1.108529 | 0.879725 | 1.082474 | 1 | 1 |
| 4.A | 3.19 | 3.59 | 3.51 | 3.51 | 3.58 | 3.81 | 4.A | 0.83727 | 0.842257 | 0.82128 | 1 | 0.887138 | 1 | 1 |
| 4.B | 3.31 | 3.76 | 3.49 | 3.75 | 3.47 | 3.87 | 4.B | 0.901807 | 1.024523 | 0.850954 | 1.021789 | 0.845504 | 1 | 1 |
| 4.C | 3.57 | 3.7 | 3.76 | 3.89 | 3.89 | 4.08 | 4.C | 0.87831 | 0.91133 | 0.828108 | 0.98128 | 0.908887 | 1 | 1 |
| 4.D | 3.57 | 3.74 | 3.58 | 3.81 | 3.54 | 3.83 | 4.D | 0.908397 | 0.951854 | 0.895852 | 0.984811 | 0.900783 | 1 | 1 |
| 4.E | 3.41 | 3.72 | 3.61 | 3.86 | 3.63 | 3.89 | 4.E | 0.848837 | 0.832331 | 0.804762 | 0.872431 | 0.809774 | 1 | 1 |
| 5.A | 3.14 | 3.4 | 3.28 | 3.21 | 3.25 | 3.53 | 5.A | 0.888518 | 0.83173 | 0.828178 | 0.808348 | 0.82058 | 1 | 1 |
| 5.B | 3.2 | 3.56 | 3.32 | 3.32 | 3.32 | 3.32 | 5.B | 0.963855 | 1.072288 | 1.060241 | 1 | 1 | 1 | 1 |
| 5.C | 3.48 | 3.54 | 3.63 | 3.67 | 3.87 | 3.58 | 5.C | 0.972087 | 0.888827 | 1.073868 | 1.02514 | 1.02514 | 1 | 1 |
| 5.D | 3.44 | 3.63 | 3.53 | 3.23 | 3.5 | 3.37 | 5.D | 1.020772 | 1.077151 | 1.047478 | 0.958457 | 1.038578 | 1 | 1 |
| 5.E | 3.24 | 3.01 | 3.21 | 2.74 | 3.23 | 2.83 | 5.E | 1.105802 | 1.027304 | 1.095583 | 0.835154 | 1.102389 | 1 | 1 |
| 6.A | 3.82 | 3.35 | 3.63 | 3.73 | 3.64 | 3.77 | 6.A | 1.013283 | 0.888594 | 1.015915 | 0.88838 | 0.985517 | 1 | 1 |
| 6.B | 3.77 | 3.8 | 3.74 | 4.05 | 3.84 | 4.07 | 6.B | 0.92829 | 0.833681 | 0.818918 | 0.865085 | 0.868778 | 1 | 1 |
| 6.C | 3.67 | 3.69 | 3.63 | 3.8 | 3.64 | 4.03 | 6.C | 0.91087 | 0.815833 | 0.800744 | 0.842823 | 0.903228 | 1 | 1 |
| 6.D | 3.71 | 3.61 | 3.72 | 3.75 | 3.81 | 3.75 | 6.D | 1.025333 | 0.862887 | 0.992 | 1 | 1.018 | 1 | 1 |
| 6.E | 3.6 | 3.18 | 3.2 | 3.88 | 3.42 | 3.88 | 6.E | 1.088331 | 1.032488 | 1.038881 | 1.253247 | 1.11039 | 1 | 1 |
| S2 aver | 3.474 | 3.894 | 3.838 | 3.604 | 3.588 | 3.82 | S2 aver | 0.888524 | 0.834864 | 0.828361 | 0.970408 | 0.910204 | 1 | 1 |
| S3 aver | 3.12 | 3.338 | 3.458 | 3.208 | 3.36 | 3.322 | S3 aver | 0.88388 | 1.004214 | 1.040839 | 0.965883 | 1.011439 | 1 | 1 |
| S4 aver | 3.41 | 3.702 | 3.588 | 3.448 | 3.542 | 3.882 | S4 aver | 0.878158 | 0.951182 | 0.921377 | 0.888895 | 0.810072 | 1 | 1 |
| S5 aver | 3.3 | 3.428 | 3.434 | 3.234 | 3.384 | 3.46 | S5 aver | 0.888252 | 1.024507 | 1.0263 | 0.986527 | 1.014345 | 1 | 1 |
| S6 aver | 3.728 | 3.528 | 3.624 | 3.838 | 3.61 | 3.74 | S6 aver | 0.899257 | 0.842781 | 0.888884 | 1.028203 | 0.865241 | 1 | 1 |
| Average | 3.4444 | 3.6312 | 3.548 | 3.5864 | 3.4848 | 3.644 | Average | 0.845225 | 0.868045 | 0.973555 | 0.884193 | 0.958058 | 1 | 1 |
| ThSDev | 0.2115435 | 0.25187338 | 0.17385339 | 0.380261752 | 0.18801323 | 0.37310633 | ThSDev | 0.566878 | 0.701873 | 0.465982 | 1.018178 | 0.608553 | 1 | 1 |
| StDev(ev) | 0.1730168 | 0.15488719 | 0.09541488 | 0.334088012 | 0.11089274 | 0.291283387 | StDev(ev) | 0.5663981 | 0.8307111 | 0.327587 | 1.146952 | 0.380704 | 1 | 1 |

ANNEX 3

ROTOR SEALING RESULTS

| Material | 934 Ref | 934 A | 934 B | 934 C | 934 D | 934 Y | RM8343 | RM8403 | MEB152 |
|-----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| Warpings | | | | | | | | | |
| Center | | | | | | | | | |
| SZE | 1.26 | 0.45 | 0.92 | 0.95 | 0.42 | 0 | 0.34 | 0 | 1.04 |
| SSE | 2.91 | 1.61 | 1.25 | 1.35 | 1.21 | 2.2 | 2.15 | 2.65 | 1.9 |
| SSE | 1.3 | 0.67 | 1.55 | 1.35 | 1.72 | 1.42 | 1.6 | 1.53 | 1.66 |
| SSE | 2.8 | 1.4 | 1.83 | 2.16 | 2.47 | 3.34 | 2.75 | 3.67 | 1.71 |
| SSE | 2.6 | 0.3 | 1.6 | 2.22 | 1.61 | 0 | 3.82 | 2.41 | 1.6 |
| WAV(32-3) | 2.172 | 0.889 | 1.43 | 1.635 | 1.864 | 1.392 | 2.112 | 2.092 | 1.882 |
| Max | | | | | | | | | |
| SZmax | 1.3 | 0.65 | 1.47 | 0.95 | 0.66 | 0.77 | 0.69 | 0.9 | 1.05 |
| SSEmax | 3.02 | 1.61 | 1.25 | 1.69 | 2.1 | 2.39 | 2.15 | 2.85 | 1.9 |
| SSEmax | 1.3 | 0.69 | 1.55 | 1.31 | 1.72 | 1.42 | 1.72 | 1.53 | 1.79 |
| SSEmax | 2.8 | 1.4 | 1.83 | 2.16 | 2.58 | 2.21 | 2.75 | 3.67 | 1.75 |
| SSEmax | 2.71 | 0.34 | 1.6 | 2.22 | 1.61 | 1.29 | 4.01 | 2.41 | 1.6 |
| WAV(32-3) | 2.228 | 0.838 | 1.44 | 1.708 | 1.754 | 1.442 | 2.284 | 2.272 | 1.828 |
| Max | | | | | | | | | |
| SZmax | 1.61 | 3.55 | 3.45 | 3.45 | 3.59 | 3.42 | 3.61 | 3.35 | 3.43 |
| SSEmax | 3.53 | 3.36 | 3.48 | 3.36 | 3.47 | 3.36 | 3.49 | 3.36 | 3.37 |
| SSEmax | 3.62 | 3.49 | 3.35 | 3.47 | 3.56 | 3.46 | 3.63 | 3.62 | 3.77 |
| SSEmax | 3.53 | 3.59 | 3.37 | 3.71 | 3.56 | 3.48 | 3.69 | 3.69 | 3.71 |
| SSEmax | 3.56 | 3.37 | 3.25 | 3.37 | 3.53 | 3.53 | 3.58 | 3.54 | 3.58 |
| SSEmax | 3.27 | 3.24 | 3.25 | 3.37 | 3.53 | 3.53 | 3.58 | 3.54 | 3.58 |
| SSEmax | 3.34 | 3.23 | 3.45 | 3.24 | 3.37 | 3.24 | 3.47 | 3.13 | 3.18 |
| SSEmax | 3.47 | 3.52 | 3.43 | 3.54 | 3.42 | 3.41 | 3.45 | 3.35 | 3.65 |
| SSEmax | 3.41 | 3.55 | 3.47 | 3.63 | 3.54 | 3.43 | 3.45 | 3.35 | 3.51 |
| SSEmax | 3.23 | 3.02 | 3.29 | 3.35 | 3.22 | 3.18 | 3.22 | 3.04 | 3.16 |
| SSEmax | 3.35 | 3.10 | 3.32 | 3.52 | 3.32 | 3.21 | 3.51 | 3.48 | 3.39 |
| SSEmax | 3.45 | 3.31 | 3.46 | 3.54 | 3.39 | 3.27 | 3.48 | 3.28 | 3.47 |
| SSEmax | 3.01 | 3.37 | 3.71 | 3.55 | 3.62 | 3.46 | 3.76 | 3.5 | 3.65 |
| SSEmax | 3.38 | 3.37 | 3.45 | 3.64 | 3.57 | 3.49 | 3.56 | 3.55 | 3.54 |
| SSEmax | 3.53 | 3.41 | 3.45 | 3.48 | 3.48 | 3.42 | 3.61 | 3.42 | 3.63 |
| SSEmax | 3.19 | 3.14 | 3.19 | 3.53 | 3.19 | 3.38 | 3.28 | 3.21 | 3.26 |
| SSEmax | 3.38 | 3.2 | 3.45 | 3.28 | 3.59 | 3.25 | 3.24 | 3.13 | 3.32 |
| SSEmax | 3.41 | 3.48 | 3.56 | 3.56 | 3.47 | 3.54 | 3.63 | 3.52 | 3.67 |
| SSEmax | 3.43 | 3.44 | 3.39 | 3.65 | 3.34 | 3.29 | 3.53 | 3.45 | 3.5 |
| SSEmax | 3.29 | 3.24 | 3.25 | 3.27 | 3.25 | 3.1 | 3.21 | 3.1 | 3.23 |
| SSEmax | 3.64 | 3.42 | 3.64 | 3.7 | 3.81 | 3.77 | 3.83 | 3.57 | 3.84 |
| SSEmax | 3.86 | 3.77 | 3.84 | 3.7 | 3.78 | 3.66 | 3.74 | 3.62 | 3.64 |
| SSEmax | 3.71 | 3.67 | 3.74 | 3.64 | 3.6 | 3.61 | 3.63 | 3.7 | 3.64 |
| SSEmax | 3.69 | 3.77 | 3.64 | 3.97 | 3.68 | 3.7 | 3.72 | 3.6 | 3.81 |
| SSEmax | 3.41 | 3.5 | 3.58 | 3.47 | 3.41 | 3.39 | 3.32 | 3.26 | 3.42 |
| SSEmax | 3.74 | 3.474 | 3.578 | 3.504 | 3.442 | 3.47 | 3.53 | 3.472 | 3.558 |
| SSEmax | 3.31 | 3.312 | 3.378 | 3.376 | 3.35 | 3.459 | 3.364 | 3.36 | 3.46 |
| SSEmax | 3.534 | 3.41 | 3.478 | 3.528 | 3.416 | 3.565 | 3.445 | 3.445 | 3.542 |
| SSEmax | 3.55 | 3.3 | 3.55 | 3.558 | 3.528 | 3.272 | 3.24 | 3.24 | 3.304 |
| SSEmax | 3.504 | 3.25 | 3.654 | 3.699 | 3.566 | 3.66 | 3.624 | 3.64 | 3.81 |
| Average | 0.17913 | 0.211544 | 0.170899 | 0.166421 | 0.169833 | 0.153577 | 0.173653 | 0.168565 | 0.189013 |
| ThSDev | 0.145096 | 0.173017 | 0.121512 | 0.104635 | 0.130115 | 0.123843 | 0.095415 | 0.127739 | 0.110993 |
| StDev(%) | 1.520683 | 1.81331 | 1.273513 | 1.06668 | 1.373103 | 1.297947 | 1.133772 | 1.162216 | 1.081769 |

RESULTS COMPARED TO RM8343

Annex 4

ROTO SERIAL 3 RESULTS

| Material | Fid. coord. | 934 Ref | 934 A | 934 B | 934 C | 934 D | 934 E | 934 F | 934 G | 934 H | 934 I | 934 J | 934 K | 934 L | 934 M | 934 N | 934 O | 934 P | 934 Q | 934 R | 934 S | 934 T | 934 U | 934 V | 934 W | 934 X | 934 Y | 934 Z | 934 AA | 934 AB | 934 AC | 934 AD | 934 AE | 934 AF | 934 AG | 934 AH | 934 AI | 934 AJ | 934 AK | 934 AL | 934 AM | 934 AN | 934 AO | 934 AP | 934 AQ | 934 AR | 934 AS | 934 AT | 934 AU | 934 AV | 934 AW | 934 AX | 934 AY | 934 AZ | 934 BA | 934 BB | 934 BC | 934 BD | 934 BE | 934 BF | 934 BG | 934 BH | 934 BI | 934 BJ | 934 BK | 934 BL | 934 BM | 934 BN | 934 BO | 934 BP | 934 BQ | 934 BR | 934 BS | 934 BT | 934 BU | 934 BV | 934 BW | 934 BX | 934 BY | 934 BZ | 934 CA | 934 CB | 934 CC | 934 CD | 934 CE | 934 CF | 934 CG | 934 CH | 934 CI | 934 CJ | 934 CK | 934 CL | 934 CM | 934 CN | 934 CO | 934 CP | 934 CQ | 934 CR | 934 CS | 934 CT | 934 CU | 934 CV | 934 CW | 934 CX | 934 CY | 934 CZ | 934 DA | 934 DB | 934 DC | 934 DD | 934 DE | 934 DF | 934 DG | 934 DH | 934 DI | 934 DJ | 934 DK | 934 DL | 934 DM | 934 DN | 934 DO | 934 DP | 934 DQ | 934 DR | 934 DS | 934 DT | 934 DU | 934 DV | 934 DW | 934 DX | 934 DY | 934 DZ | 934 EA | 934 EB | 934 EC | 934 ED | 934 EE | 934 EF | 934 EG | 934 EH | 934 EI | 934 EJ | 934 EK | 934 EL | 934 EM | 934 EN | 934 EO | 934 EP | 934 EQ | 934 ER | 934 ES | 934 ET | 934 EU | 934 EV | 934 EW | 934 EX | 934 EY | 934 EZ | 934 FA | 934 FB | 934 FC | 934 FD | 934 FE | 934 FF | 934 FG | 934 FH | 934 FI | 934 FJ | 934 FK | 934 FL | 934 FM | 934 FN | 934 FO | 934 FP | 934 FQ | 934 FR | 934 FS | 934 FT | 934 FU | 934 FV | 934 FW | 934 FX | 934 FY | 934 FZ | 934 GA | 934 GB | 934 GC | 934 GD | 934 GE | 934 GF | 934 GH | 934 GI | 934 GJ | 934 GK | 934 GL | 934 GM | 934 GN | 934 GO | 934 GP | 934 GQ | 934 GR | 934 GS | 934 GT | 934 GU | 934 GV | 934 GW | 934 GX | 934 GY | 934 GZ | 934 HA | 934 HB | 934 HC | 934 HD | 934 HE | 934 HF | 934 HG | 934 HH | 934 HI | 934 HJ | 934 HK | 934 HL | 934 HM | 934 HN | 934 HO | 934 HP | 934 HQ | 934 HR | 934 HS | 934 HT | 934 HU | 934 HV | 934 HW | 934 HX | 934 HY | 934 HZ | 934 IA | 934 IB | 934 IC | 934 ID | 934 IE | 934 IF | 934 IG | 934 IH | 934 II | 934 IJ | 934 IK | 934 IL | 934 IM | 934 IN | 934 IO | 934 IP | 934 IQ | 934 IR | 934 IS | 934 IT | 934 IU | 934 IV | 934 IW | 934 IX | 934 IY | 934 IZ | 934 JA | 934 JB | 934 JC | 934 JD | 934 JE | 934 JF | 934 JG | 934 JH | 934 JI | 934 JJ | 934 JK | 934 JL | 934 JM | 934 JN | 934 JO | 934 JP | 934 JQ | 934 JR | 934 JS | 934 JT | 934 JU | 934 JV | 934 JW | 934 JX | 934 JY | 934 JZ | 934 KA | 934 KB | 934 KC | 934 KD | 934 KE | 934 KF | 934 KG | 934 KH | 934 KI | 934 KJ | 934 KK | 934 KL | 934 KM | 934 KN | 934 KO | 934 KP | 934 KQ | 934 KR | 934 KS | 934 KT | 934 KU | 934 KV | 934 KW | 934 KX | 934 KY | 934 KZ | 934 LA | 934 LB | 934 LC | 934 LD | 934 LE | 934 LF | 934 LG | 934 LH | 934 LI | 934 LJ | 934 LK | 934 LL | 934 LM | 934 LN | 934 LO | 934 LP | 934 LQ | 934 LR | 934 LS | 934 LT | 934 LU | 934 LV | 934 LW | 934 LX | 934 LY | 934 LZ | 934 MA | 934 MB | 934 MC | 934 MD | 934 ME | 934 MF | 934 MG | 934 MH | 934 MI | 934 MJ | 934 MK | 934 ML | 934 MM | 934 MN | 934 MO | 934 MP | 934 MQ | 934 MR | 934 MS | 934 MT | 934 MU | 934 MV | 934 MW | 934 MX | 934 MY | 934 MZ | 934 NA | 934 NB | 934 NC | 934 ND | 934 NE | 934 NF | 934 NG | 934 NH | 934 NI | 934 NJ | 934 NK | 934 NL | 934 NM | 934 NO | 934 NP | 934 NQ | 934 NR | 934 NS | 934 NT | 934 NU | 934 NV | 934 NW | 934 NX | 934 NY | 934 NZ | 934 OA | 934 OB | 934 OC | 934 OD | 934 OE | 934 OF | 934 OG | 934 OH | 934 OI | 934 OJ | 934 OK | 934 OL | 934 OM | 934 ON | 934 OO | 934 OP | 934 OQ | 934 OR | 934 OS | 934 OT | 934 OU | 934 OV | 934 OW | 934 OX | 934 OY | 934 OZ | 934 PA | 934 PB | 934 PC | 934 PD | 934 PE | 934 PF | 934 PG | 934 PH | 934 PI | 934 PJ | 934 PK | 934 PL | 934 PM | 934 PN | 934 PO | 934 PP | 934 PQ | 934 PR | 934 PS | 934 PT | 934 PU | 934 PV | 934 PW | 934 PX | 934 PY | 934 PZ | 934 QA | 934 QB | 934 QC | 934 QD | 934 QE | 934 QF | 934 QG | 934 QH | 934 QI | 934 QJ | 934 QK | 934 QL | 934 QM | 934 QN | 934 QO | 934 QP | 934 QQ | 934 QR | 934 QS | 934 QT | 934 QU | 934 QV | 934 QW | 934 QX | 934 QY | 934 QZ | 934 RA | 934 RB | 934 RC | 934 RD | 934 RE | 934 RF | 934 RG | 934 RH | 934 RI | 934 RJ | 934 RK | 934 RL | 934 RM | 934 RN | 934 RO | 934 RP | 934 RQ | 934 RR | 934 RS | 934 RT | 934 RU | 934 RV | 934 RW | 934 RX | 934 RY | 934 RZ | 934 SA | 934 SB | 934 SC | 934 SD | 934 SE | 934 SF | 934 SG | 934 SH | 934 SI | 934 SJ | 934 SK | 934 SL | 934 SM | 934 SN | 934 SO | 934 SP | 934 SQ | 934 SR | 934 SS | 934 ST | 934 SU | 934 SV | 934 SW | 934 SX | 934 SY | 934 SZ | 934 TA | 934 TB | 934 TC | 934 TD | 934 TE | 934 TF | 934 TG | 934 TH | 934 TI | 934 TJ | 934 TK | 934 TL | 934 TM | 934 TN | 934 TO | 934 TP | 934 TQ | 934 TR | 934 TS | 934 TT | 934 TU | 934 TV | 934 TW | 934 TX | 934 TY | 934 TZ | 934 UA | 934 UB | 934 UC | 934 UD | 934 UE | 934 UF | 934 UG | 934 UH | 934 UI | 934 UJ | 934 UK | 934 UL | 934 UM | 934 UN | 934 UO | 934 UP | 934 UQ | 934 UR | 934 US | 934 UT | 934 UV | 934 UW | 934 UX | 934 UY | 934 UZ | 934 VA | 934 VB | 934 VC | 934 VD | 934 VE | 934 VF | 934 VG | 934 VH | 934 VI | 934 VJ | 934 VK | 934 VL | 934 VM | 934 VN | 934 VO | 934 VP | 934 VQ | 934 VR | 934 VS | 934 VT | 934 VU | 934 VV | 934 VW | 934 VX | 934 VY | 934 VZ | 934 WA | 934 WB | 934 WC | 934 WD | 934 WE | 934 WF | 934 WG | 934 WH | 934 WI | 934 WJ | 934 WK | 934 WL | 934 WM | 934 WN | 934 WO | 934 WP | 934 WQ | 934 WR | 934 WS | 934 WT | 934 WU | 934 WV | 934 WW | 934 WX | 934 WY | 934 WZ | 934 XA | 934 XB | 934 XC | 934 XD | 934 XE | 934 XF | 934 XG | 934 XH | 934 XI | 934 XJ | 934 XK | 934 XL | 934 XM | 934 XN | 934 XO | 934 XP | 934 XQ | 934 XR | 934 XS | 934 XT | 934 XU | 934 XV | 934 XW | 934 XX | 934 XY | 934 XZ | 934 YA | 934 YB | 934 YC | 934 YD | 934 YE | 934 YF | 934 YG | 934 YH | 934 YI | 934 YJ | 934 YK | 934 YL | 934 YM | 934 YN | 934 YO | 934 YP | 934 YQ | 934 YR | 934 YS | 934 YT | 934 YU | 934 YV | 934 YW | 934 YX | 934 YY | 934 YZ | 934 ZA | 934 ZB | 934 ZC | 934 ZD | 934 ZE | 934 ZF | 934 ZG | 934 ZH | 934 ZI | 934 ZJ | 934 ZK | 934 ZL | 934 ZM | 934 ZN | 934 ZO | 934 ZP | 934 ZQ | 934 ZR | 934 ZS | 934 ZT | 934 ZU | 934 ZV | 934 ZW | 934 ZX | 934 ZY | 934 ZZ |
|----------|-------------|---------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|----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|----------|-------------|---------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|----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Claims

1. A polymer composition suitable for rotomoulding comprising

I) an ethylene homopolymer or copolymer with at least one other C₃₋₁₀ α -olefin, having a melt flow rate of 0.5 to 30, a molecular weight distribution (Mw/Mn) of less than 4, an Mw of 50,000 to 110,000, a density of 0.940 g/cm³ to 0.970 g/cm³ and a melting point of 100 to 145°C;

OR

II) a propylene homopolymer or copolymer with at least one other C₂₋₁₀ α -olefin, having a melt flow rate of 0.5 to 30, a molecular weight distribution (Mw/Mn) of less than 4, an Mw of 150,000 to 300,000, and a melting point of 100 to 170°C;

and

III) an ethylene homo or copolymer with at least one other C₃₋₁₀ α -olefin, having a melt flow rate of within 40% of the melt flow rate of component (I), a molecular weight distribution of (Mw/Mn) of less than 4, an Mw of within 30% of the Mw of component (I), a density of 0.880 g/cm³ to 0.940 g/cm³ said density being at least 0.010 g/cm³ less than the density of component (I) and a melting point of at least 5°C less than that of component (I);

OR

IV) a propylene homo or copolymer with at least one other C₂₋₁₀ α -olefin having a melt flow rate of within 40% of the melt flow rate of component (I), a molecular weight distribution of (Mw/Mn) of less than 4, an Mw of within 30% of the Mw of component (I), and a melting point of at least 10°C less than that of component (I).

2. A polymer composition as claimed in claim 1 comprising

I) an ethylene homopolymer having a melt flow rate of 0.5 to 30, a molecular weight distribution (Mw/Mn) of less than 4, an Mw of 50,000 to 110,000, a density of 0.940 g/cm³ to 0.970 g/cm³ and a melting point of 100 to 145°C;

and

II) an ethylene copolymer with at least one C₃₋₁₀ α -olefin having a melt flow rate of within 40% of the melt flow rate of component (I), a molecular weight distribution of (Mw/Mn) of less than 4, an Mw of within 30% of the Mw of component (I), a density of 0.880 g/cm³ to 0.940 g/cm³ said density being at least 0.010 g/cm³ less than the density of component (I) and a melting point of at least 10°C less than that of component (I).

3. A composition as claimed in claim 2 wherein component (II) is an ethylene copolymer with butene, hexene or octene.

4. A composition as claimed in claim 3 wherein component (II) is an ethylene copolymer with hexene.

5. A composition as claimed in any one of claims 2 to 4 wherein the melt flow rates of components (I) and (II) are 4 to 10.

6. A composition as claimed in claims 5 wherein the melt flow rates of components (I) and (II) are 6 to 8.

7. A composition as claimed in any one of claims 2 to 6 wherein the molecular weight distribution of the composition is less than 4.

8. A composition as claimed in any one of claims 2 to 7 wherein the density of component (II) is 0.910 g/cm³ to 0.930 g/cm³.9. A composition as claimed in any one of claims 2 to 8 wherein the density of composition is in the range 0.925 to 0.950 g/cm³.10. A composition as claimed in claim 9 wherein the density of composition is in the range 0.930 to 0.940 g/cm³.

11. A composition as claimed in any one of claims 2 to 10 wherein the melting point of component (I) is in the range 125°C to 135°C and the melting point of component (II) is in the range 100°C to 125°C.

12. A composition as claimed in any one of claims 1 to 11 wherein the molecular weight distribution each of components

(I) and (II) is less than 3.

13. A composition as claimed in claim 1 comprising

- 5 I) a propylene homopolymer having a melt flow rate of 4 to 10; a molecular weight distribution (Mw/Mn) of less than 4, an Mw of 150,000 to 300,000, and a melting point of 100 to 170°C;
and
- 10 II) a propylene homopolymer having a melt flow rate of within 40% of the melt flow rate of component (I), a molecular weight distribution of (Mw/Mn) of less than 4, an Mw of within 30% of the Mw of component (I), and a melting point of at least 10°C less than that of component (I);

wherein said composition has a molecular weight distribution (Mw/Mn) of less than 4.

15 14. A composition as claimed in claim 13 wherein component (II) is amorphous.

15. A composition as claimed in any one of claims 1 to 14 wherein the ratio of component (I) to (II) is from 4:1 to 1:4.

20 16. The use of a polymer composition as claimed in any one of claims 1 to 15 in rotomoulding.

17. A process for the preparation of an article comprising rotomoulding a composition as claimed in any one of claims 1 to 15.

25 18. A process as claimed in claim 17 wherein rotomoulding is effected at a rotation speed of 9/1.4 RPM; heating for 13 minutes in oven at 270°C; fan assisted cooling for 10 minutes followed by 6 minutes ambient cooling in the absence of a fan.

19. An article comprising a polymer composition as claimed in any one of claims 1 to 15.

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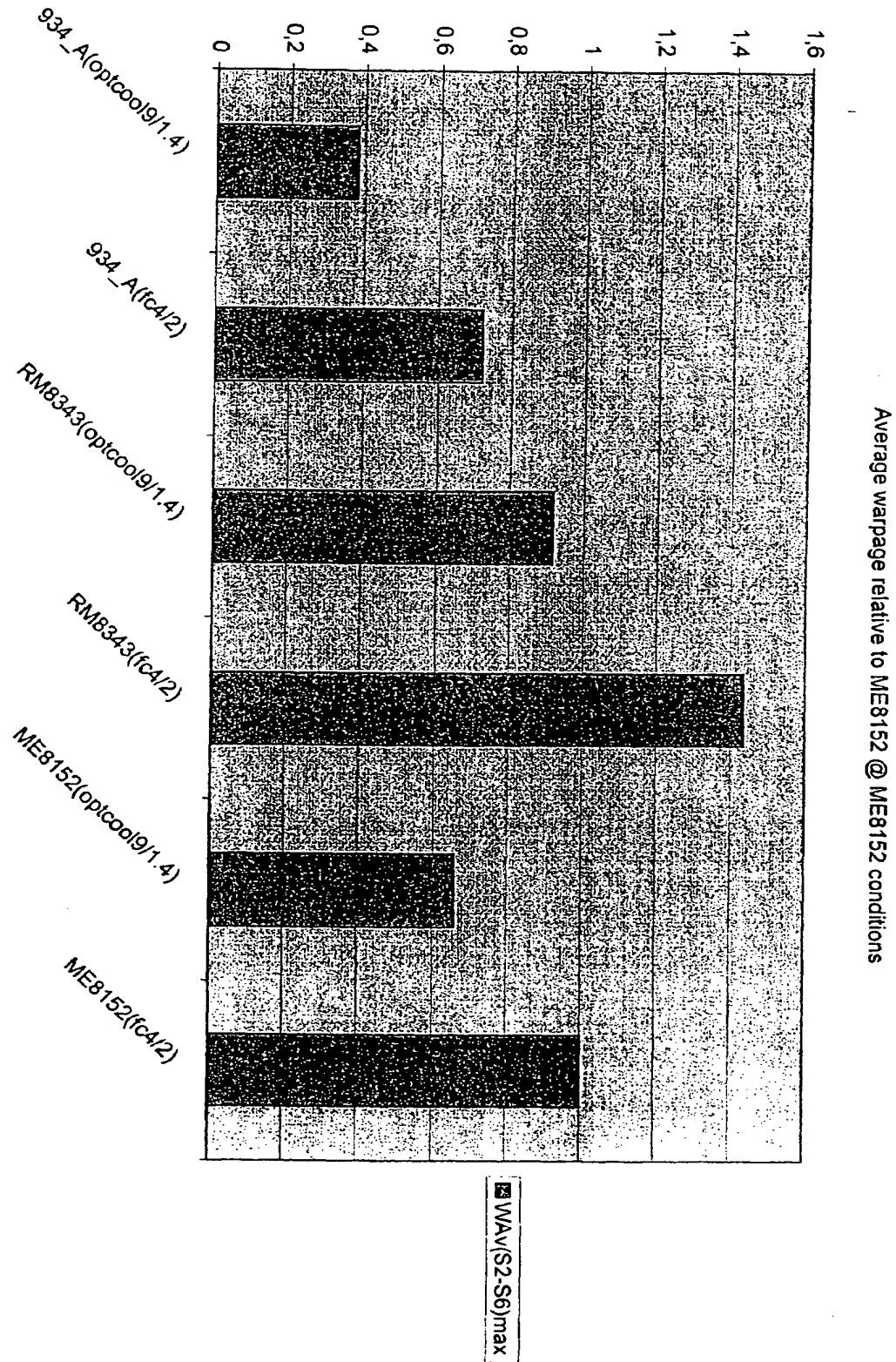
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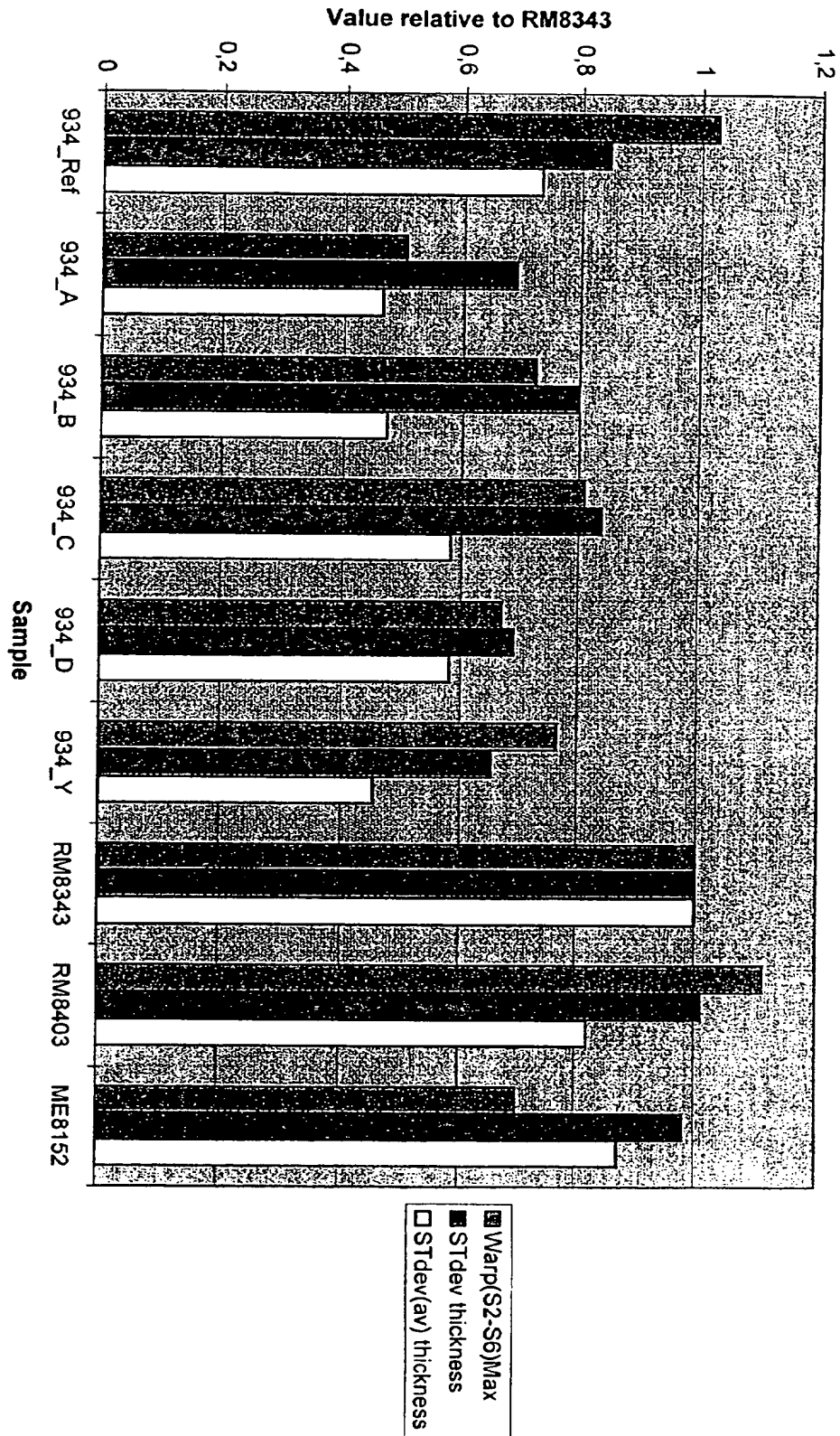
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Full cooling/4:2 rotation





European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 01 30 1873

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| <p>The present search report has been drawn up for all claims</p> | | | |
| Place of search THE HAGUE | | Date of completion of the search 7 August 2001 | Examiner SCHMIDT, H |
| <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background G : non-written disclosure P : intermediate document</p> | | <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons S : member of the same patent family, corresponding document</p> | |

EPO FORM 1503 03 82 (P04C01)



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CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

- ☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- ☒ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

1, 5, 6, 7, 11, 12, 15 - 19 partially, 2, 3, 4, and 8 - 10



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Office

**LACK OF UNITY OF INVENTION
SHEET B**

Application Number
EP 01 30 1873

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims: 1, 5, 6, 7, 11, 12, 15-19 partially, 2, 3, 4,
and 8-10

as far as compositions of polyethylene I) with polymer II)
are concerned

2. Claims: 1, 5, 6, 7, 11, 12, 15-19 partially 13, 14

as far as compositions of polypropylene I) with polymer II)
are concerned

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 30 1873

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The members are as contained in the European Patent Office EDP file on
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